UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

AD-A205 570

1b. RESTRICTIVE MARKINGS	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution is unlimited.
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S): AFOSR-TR- 89-0309
6a. NAME OF PERFORMING ORGANIZATION: Yale University; 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION: AFOSR/NC
6c. ADDRESS (City, State, and ZIP Code): New Haven, CT 06520-2159	7b. ADDRESS (City, State, and ZIP Code): Building 410, Bolling AFB DC 20332-6448
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: AFOSR; 8b. OFFICE SYMBOL (If applicable): NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: AFOSR-87-0323
8c. ADDRESS (City, State, and ZIP Code): Building 410, Bolling AFB DC 20332-6448	10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO.
61102F	2303	B1	

11. TITLE (Include Security Classification)
(U) SPECTROMETRIC STUDIES OF GAS PHASE COLLISION PROCESSES

12. PERSONAL AUTHOR(S) J. B. Fenn

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final Report	FROM 8/1/87 TO 7/31/88	February 10, 1989	

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Free jets, Gas Dynamics, Infrared Spectrometry, Rotational relaxation, Super-radiance, Collisions, Phase studies, vapor phases. (AW)

19. ABSTRACT (Continue on reverse if necessary and identify by block number) (Carbon monoxide) (Carbon dioxide) (Carbon

Measurements have been made of the total radiation intensity from free jets of CO_2 and CO that were excited in the source by a corona discharge. The radiation per molecule, obtained from the ratio of total intensity to source density, increases sharply when source temperature and pressure are such as to produce clustering in a jet of unexcited gas. We believe this enhancement may be due to interaction between aligned dipoles in adjacent cluster molecules. Measurements of the terminal rotational "temperature" of CO and CO_2, both pure in admixture with each other and/or argon indicate that CO always relaxes more slowly. There is no evidence of coupling between the rotational modes of the two species. Keywords:

DTIC ELECTE 13 MAR 1989 S E

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT: ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION: UNCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL: F J WODARCZYK	22b. TELEPHONE (Include Area Code): (202) 767-4963; 22c. OFFICE SYMBOL: AFOSR/NC

DD Form 1473, JUN 86 Previous editions are obsolete. SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

AFOSR-TR- 89-0308

Spectrometric Studies of Gas Phase Collision Processes

AFOSR Contract F49620-87-0323

J. B. Fenn, Principal Investigator

Final Report
8/1/87-7/31/88

I. Introduction-Objectives

This report covers results obtained from experiments in our laboratory over the indicated period. Though it was performed under the aegis of a new one year contract, the work was in effect an extension of the research that had been carried out for the preceding three year period under AFOSR Contract F49620-85-C-0065. For a summary and review of that research, reference is made to the final report on that contract which was submitted on 12/15/87. The original objective of the research reported here was to document further an anomalous enhancement in the infrared radiation that had been observed from a free jet of carbon dioxide that been excited in the source by a corona discharge. We achieved that objective and in addition obtained some information on rotational relaxation in mixtures of carbon dioxide and carbon monoxide.

II. Achievements and Results

(1) Superradiance. In some earlier studies we had characterized the terminal rotational state of gas that had undergone supersonic free jet expansion from a small nozzle into vacuum. Our diagnostic method was based on analysis of the radiation from this terminal gas by Fourier Transform Infrared Spectrometry (FTIS). Because their radiation is at wavelengths for which IR detectors are most sensitive we used carbon monoxide and carbon dioxide in the jet gas. The vibrational excitation necessary for radiation was achieved in those early experiments simply by raising the temperature of the source gas. A noteworthy finding was that rotational energy in this terminal state showed marked departures from a Boltzmann distribution. Moreover, the extent of these departures increased as the terminal jet temperature decreased. In order to determine whether this trend would continue with further decreases in terminal jet temperature we tried using a corona discharge to excite vibration in the source gas without putting much energy into the rotational and translational modes. We found that the departures from a Boltzmann distribution continued to increase until condensation set in.

A much more interesting finding was the focus of the present study. When the source gas pressure was increased, or its temperature decreased, there was a sudden and marked enhancement of intensity from the asymmetric stretch mode in carbon dioxide when the source temperature and pressure reached values at which condensation would be expected to occur during the expansion. The enhancement amounts to as much as a five-fold increase in the radiation per molecule, i.e. a fivefold decrease in radiation lifetime. Similar results with carbon monoxide have now been obtained. We first thought that the enhancement might be due to stimulated emission made possible by a population inversion resulting from depopulation of the lower state by condensation. However, by comparing radiation intensity with and without a mirror behind the jet we have been able to disqualify that explanation. The most likely explanation now seems to be that when an excited molecule tries to form a dimer with another molecule there is an alignment of the dipoles that enhances the radiation probability by a mechanism akin to that recently analyzed by Liver et al. (1) A note on this work is about done and will be submitted to Chemical Physics Letters. A more complete paper will be prepared for submission to the Journal of Chemical Physics or the Journal of Physical Chemistry after we complete some measurements now in progress.

(2) <u>Rotational Relaxation.</u> In developing the microjet burner, which was described in the final report for the preceding grant referenced in the Introduction, we found that the CO in the combustion products had a substantially lower rotational temperature than did the CO2. (2) It was important to determine whether this difference reflected a similar difference due to non-equilibrium in the source gas (e.g. because the CO was a "hot" intermediate) or whether it was due simply to a slower relaxation of rate for CO during the free jet expansion. Consequently, we carried out an extended study of terminal rotational energy distributions for CO and CO2, alone and in admixture with each other and/or argon. Vibrational excitation to provide emission spectra was achieved both by raising the temperature of the source gas and by means of a corona discharge. In every case the terminal rotational "temperature" of CO was substantially higher. Moreover, there was no evidence of any coupling between the rotational modes of the two gases when they were both present in a mixture. We thus conclude that the results with the burner were not indicative of any difference in the source gas before it expanded in the free jet. The results were presented at the 16th Symposium on Rarefied Gas Dynamics in Pasadena, July 1988, and will be included in proceedings. A preprint copy accompanies this report.

III. References.

(1) N. Liver, A. Nitzan, A. Amirav and J. Jortner, J. Chemical Phys. (1988) 88, 3516.

(2) W. Groeger and J. B. Fenn, Rev. Sci. Instrum.(1988) 59,1971

IV. Professional Personnel

Principal Investigator: Professor John B. Fenn

Research Associate: Takeshi Kodama who was visiting for 18 months from the Technical Research Department of Komatsu, Ltd., Japan.

Graduate Student: Shida Shen who completed his doctoral research on this project and will receive his Ph.D. in June 1989

V. Cumulative List of Publications

Included are those which were cited in the Final Report of the preceding grant as having been submitted and which have now been published. Six copies of reprints for the first two and one preprint copy of the third accompany this report. Also included are prospective papers that are in various stages of preparation.

"Microjet Burners for Molecular-beam Sources and Combustion Studies," Wolfgang Groeger and John B. Fenn, Rev. Sci. Instrum. (1988) 59, 1971.

"Internal Energy Distribution of OCS Desorbing from a Hot Platinum Surface," Wolfgang Groeger and John B. Fenn, J. Phys.-Chem. (1989) 93, 344.

"Rotational Relaxation of CO and CO2 in Free Jets of Gas Mixtures," Takeshi Kodama, Shida Shen and John B. Fenn, AIAA Series in Aeronautics and Astronautics, in press.

"Superradiance in Free Jets of Discharge-Excited CO2," Shida Shen and J. B. Fenn. In preparation for Chem. Phys. Lett.

"Gas Dynamic Modulation of Free Jet Beams," Shida Shen and J. B. Fenn. In preparation for Rev. Sci. Instrum.

"Terminal Distributions of Internal Energy in Free Jets of Discharge Excited CO and CO2." In preparation for J. Phys.Chem.